Surface Water pCO_2 Measurements from Ships

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Project Summary:

The oceans are the largest sustained sink of anthropogenic carbon taking up on average about 1.6 10^{15} gram (= 1.6 gigaton) of carbon each year. Changes in this sink will be determined by monitoring regional and seasonal patterns of carbon uptake and release. Determination of regional sources and sinks of carbon dioxide in the ocean are of critical importance to international policy decision making, as well as for forecasting long term climate trends. In this project NOAA investigators and academic partners are outfitting research and commercial vessels with automated carbon dioxide analyzers as well as thermosalinographs (TSGs) to measure the temperature, salinity and partial pressure of CO_2 (pCO_2) in surface water and air in order to determine the carbon exchange between the ocean and atmosphere. While this is the largest coordinated effort, it is by no means the only one. Success in constraining the sources and sinks depends critically on international coordination and partnerships. This task is coordinated at national level with the U.S. Carbon Cycle Science Program and its subcommittee on Ocean Carbon and Climate change (OCCC). We work with the International Ocean Carbon Coordination Project (IOCCP) for international coordination. Collaborative efforts are underway to combine datasets in the Atlantic through a Memorandum of Understanding with the European Union project CarboOcean. Pacific collaboration is established through the PICES working group 13. In addition there are one-on-one interactions with investigators in Norway, Iceland, France, the United Kingdom, Australia, New Zealand, and Japan on reciprocal data exchange and logistics support.

Documenting carbon sources and sinks relies critically on other efforts undertaken under sponsorship of the Office of Climate Observations (OCO) including implementation of the ship lines, and moored and drifting buoys. The surface water pCO_2 programs support climate services by providing knowledge and quantification of the radiatively important gas, carbon dioxide. The near-term focus is on completion of the Northern Hemisphere ocean carbon observing system to provide data for quantifying carbon dioxide sources and sinks over the coterminous United States through inverse modeling in collaboration with scientists involved in the atmospheric CO_2 observing system.

The project is a partnership of AOML, AOML/GOOS, PMEL, LDEO of Columbia University, RSMAS of the University of Miami, and the Bermuda Institute of Ocean Sciences (BIOS), formerly known as the Bermuda Biological Station for Research (BBSR). The partners are responsible for operation of the pCO_2 systems on the ships, auxiliary

measurements, data reduction, and data management from all ships. The following ships had pCO_2 systems on them during part or all of the performance period : NOAA ship *Ronald H. Brown*, NOAA ship *Ka'imimoana*, container ship *Albert* Rickmers, RVIB *Palmer*, cruise ship *Explorer of the Seas*, container ship Skogafoss container ship *Oleander*, and UNOLS research ship RV *Atlantic Explorer* (ship owned and operated by BIOS). As mentioned in the progress report and workplan several ships were taken off lines and several new ships were outfitted in the past year. The final datasets are combined and sent to CDIAC for dissemination and archival. All work follows established principles of monitoring climate forcing gases and biogeochemical cycles.

FY 2007 Progress:

Acquisitions, deployments and data return:

The main metric for this program is obtaining, reducing, quality controlling and disseminating high quality surface water and marine air pCO_2 data. The number of cruises with pCO_2 observations from research ships and VOS that have been completed during the performance period are listed in *Table **1***. Details for each ship are provided below.

SHIP	# Cruises	# Data Points	% Recovery*
R/V Brown	8	34,583	96.0%
M/V Skogafoss	11	55,588	81.0%
Explorer of the Seas	48	72,918	79.0%
RVIB Palmer	3	48,524	98.0%
R/V Ka'imimoana	5	115,334	91.0%
R/V Atlantic Explorer	16 months	92,000	83.0%
M/V Albert Rickmers	1	7,571	91.0%
M/V Oleander	12 months	108,000	68.0%

Table 1:VOS Data Summary FY-2007.

* The values are to illustrate overall performance of the program. They should be used with caution when making ship to ship comparisons. The number of data points is a function of frequency of measurements, number of cruises and instrument malfunction that differ for each ship. Percent recovery has been determined in different fashion by each investigator ranging from number of data points that could have been obtained if the units had operated whenever the ship was at sea to number of acquired data points that were discarded during quality control.

Four other critical endeavors in support of determining regional fluxes have been completed during the performance period:

1. To assure uniformity in measurements and to expand the effort within NOAA OCO and beyond, a technology transfer has been done in which General Oceanics Inc. of Miami, FL is building the underway pCO_2 systems to our specifications. Substantial time and effort is involved by participants at AOML and RSMAS to assist in building, troubleshooting, improving instrument design and training customers on the operation of the system. Over

13 units have been produced and sold to customers around the world. So far, about 6 of these units have been purchased by participants of the NOAA program.

2. The GOOS/TSG (thermosalinograph) component lead by Gustavo Goni currently operates and maintains TSGs in four ships of the SOOP: Albert Rickmers, Explorer of the Seas, M/V Explorer and Oleander. The Explorer of the Seas operations is a joint collaboration between NOAA/AOML and the University of Miami (RSMAS). We have recently successfully tested real-time mode quality control procedures for TSG data obtained from these ships. Three of these ships (Rickmers, Oleander and M/V Explorer) operate with SEAS2000 software to acquire and transmit the data in real- and delayed-time modes ().

The operations in the Skogaffoss that transected between Boston and Iceland ended in May 2007, and its data were processed and transmitted until that date. Once the replacement for this ship is found and the new TSG installed, we will resume with the data transmission in this transect.

NOAA/AOML installed a TSG unit in the M/V Explorer of the Semester At Sea Program that is operated by the University of Virginia. The first phase of this operation has been finished with the complete installation. The second phase that involves the data transmission is under progress. This ship performs two around the world transects every year. This TSG unit will support a pCO2 unit that is anticipated on this same ship.

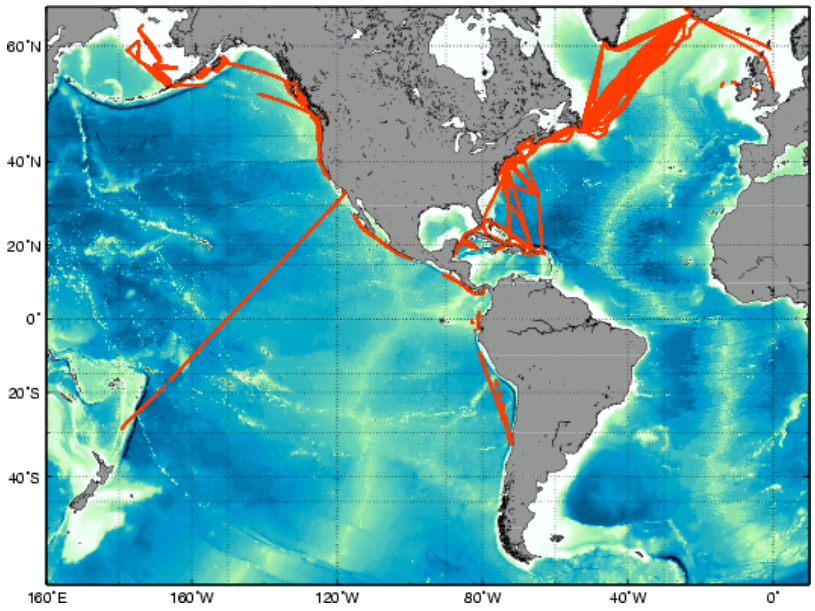

Figure 1: Location of real-time TSG transmissions into the GTS during FY 2007.

3. In addition to leading the effort on the *Palmer* the LDEO group has provided two critical data packages towards to overall goal of this project. The data produced by the NOAA-supported groups as well as those from international collaborators from Japan, Iceland, Germany and France, were processed into a single format at the Lamont-Doherty

Observatory. A compilation of all coastal data was assembled that is the cornerstone of an assessment of the role of the coastal ocean in carbon dynamics (Chavez and Takahashi, 2007). The comprehensive dataset that was used to create the global pCO_2 climatology comprised of 3.3 million data points from over a dozen research groups was sent to the Carbon Dioxide Information and Analysis Center (CDIAC) at the Oak Ridge National Laboratory, for the permanent archive and ready access to the public. The new data will be accessible only to the 25 co-authors of the paper until the paper in Deep-Sea Research is published , and will be released to the public after this period.

4. The RSMAS group jointly maintains the pCO_2 system on the *Skogafoss* and has analyzed discrete surface samples for Total Alkalinity (TA) and Total Inorganic Carbon (TC) that have been collected on select cruises. These state variables provide the opportunity to further elucidate the factors that control the surface water pCO_2 and can provide a physical basis for the CO_2 flux map analysis.

A pCO_2 system was lent to Prof. Brain Ward of Old Dominion to outfit a cruise in the North Atlantic. This high-resolution data set augments our high latitude data. We continue close interactions with the University of Bergen in data exchange for the North Atlantic and interpretation to improve flux maps in this region (e.g Chierici et al., 2007) .

The AOML group also installed a pCO_2 system on the Chinese icebreaker *Snow Dragon (Xue Long)* as part of a collaboration with the Third Institute of Oceanography in the People's Republic of China. The data will be transmitted directly to AOML and posted in near-real time on the web.

The responsibilities of the different groups are summarized in the flow diagram below.

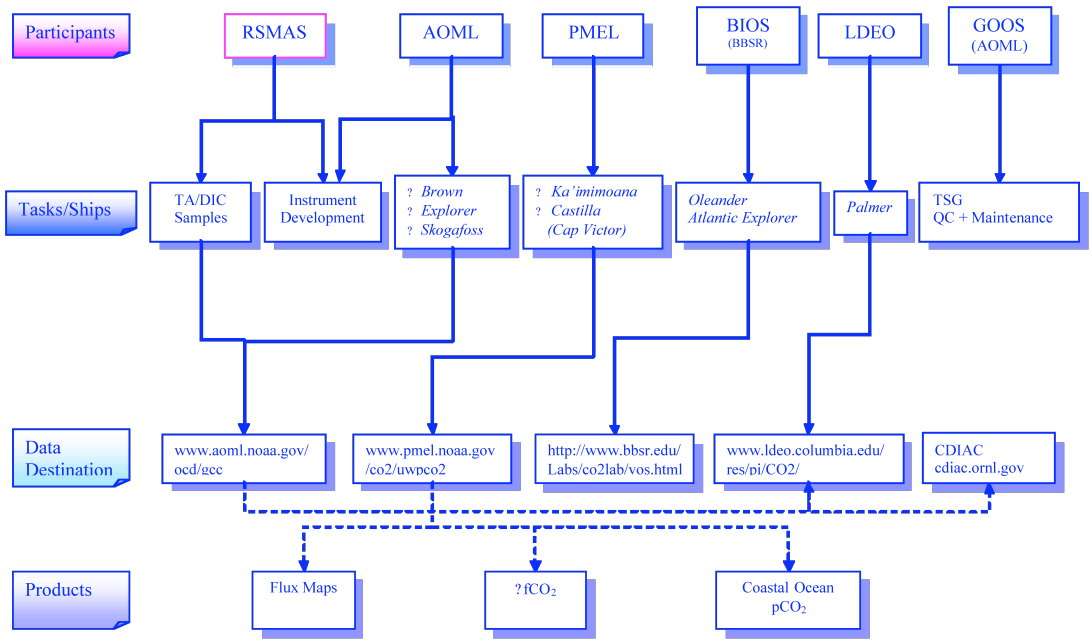

Figure 2: Organizational chart of the VOS project.

A short summary of the efforts on each ship are listed below:

***NOAA* ship *Ronald H. Brown*- AOML lead**

Causes for non-return: The underway pCO_2 system on the *Brown* enjoyed over a 96 % data return. A trip had to be made to Puerto Rico to replace the computer and failure of the air pump caused a loss of atmospheric data over a short period of time. Overall returns from the ship continue to be excellent (see *Table **1***)

Description: The cruise tracks for each cruise of the *Brown* for FY 2006 and FY 2007 are shown at http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2006.php . The cruises include the Gulf of Mexico and East Coast Carbon (GOMECC) cruise, which is the first in a biennial series planned to study the coastal region along the Gulf of Mexico and eastern seabord of North America. *Figure* ***3*** shows the pCO_2 along the cruise. The goal of this program is to reduce the large uncertainties in the carbon flux of the coastal oceans.

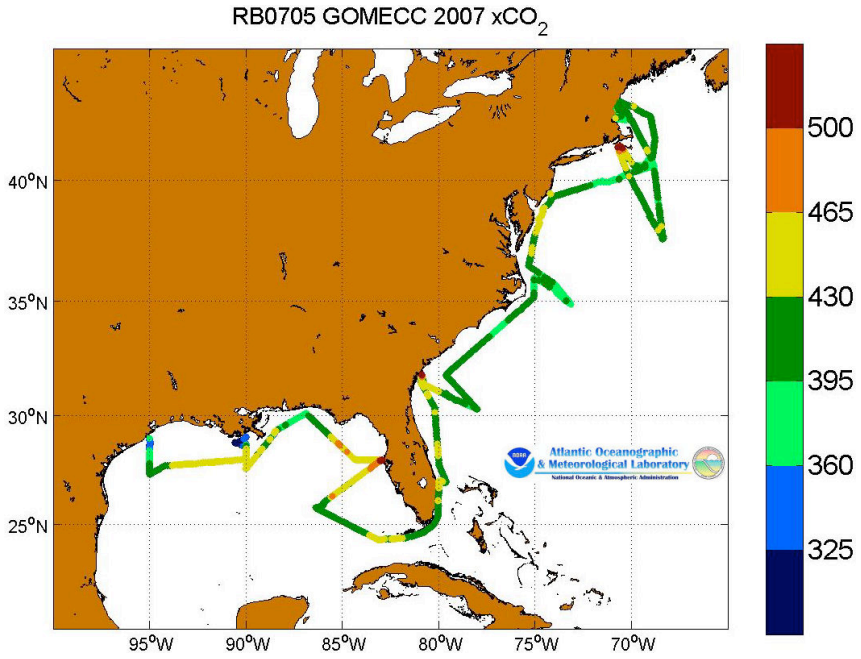

Figure 3: GOMECC cruise track and surface pCO_2 values.

NOAA ship *Ka'imimoana*- PMEL lead

Data Site: http://www.pmel.noaa.gov/co2/uwpCO2
Number of cruises: 5
Number of pCO_{2w} data points: 115334
% Data return: 91%.

Causes for non-return: The underway pCO_2 system on the *Ka'imimoana* yielded a 91 % data return during 2006-2007. There were problems associated with inadequate flushing

time prior to equilibrator measurements, resulting in rejection of a small fraction of the seawater pCO_2 values.

Description: During 2006-2007 the *Ka'imimoana* was involved in studies in the Equatorial Pacific between 95°W and 165°E (***Figure 4*****Error! Reference source not found.**). Prior to the 2006-2007 field season, the pCO_2 system was overhauled with updated software, pumps and filters. From April 2007 through September 2007, PMEL collected and processed 115,334 pCO_2 data values from the Ka'imimoana on 5 separate cruises in the equatorial Pacific. The cruise data can be obtained from our website located at**:** http://www.pmel.noaa.gov/co2/uwpco2. A summary of the cruise results from November 1997 through August 2007 is shown in ***Figure 6*****Error! Reference source not found.**. The results show weak seasonal and strong interannual variability of CO_2 fluxes from the oceans to the atmosphere. The following data files have been submitted to LDEO for contextual checks: KA0701, KA0702, KA0703, KA0704, KA0705, after which they will be submitted to CDIAC for archiving.

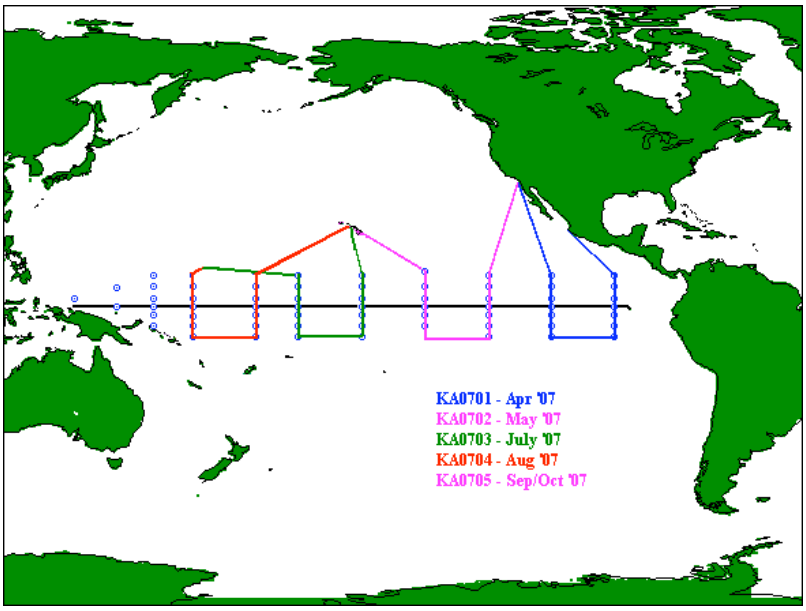

Figure 4: Ka'imimoana track lines occupied during FY 2007.

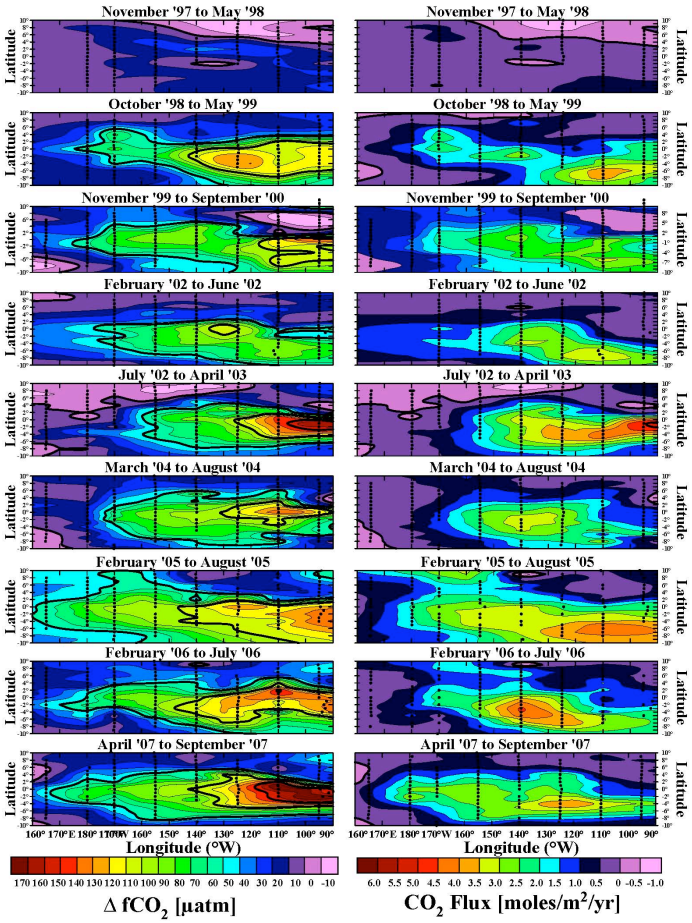

Figure 6: Time-Series of surface water pCO_2 levels in the tropical Pacific resulting from Ka'imimoana repeat observations from 1997 thru 2007.

Container ship *Albert Rickmers* - PMEL lead

Data Site: http://www.pmel.noaa.gov/co2/uwpCO2
Number of cruises: 1
Number of pCO_{2w} data points: 7571
% Data return: 91%.

Causes for non-return: The underway pCO_2 system on the *Albert Rickmers* resulted in a 91% data return during 2007. There were problems associated with inadequate flushing time prior to equilibrator measurements, resulting in rejection of a small fraction of the seawater pCO2 values.

Description: During the fall of 2007, a pCO_2 system was deployed on the container ship *Albert Rickmers*. The *Albert Rickmers* is involved in studies in the tropical and subtropical Pacific (**Error! Reference source not found.**). This research is done in collaboration with Drs. Paul Quay of the University of Washington and Bronte Tilbrook of the CSIRO in Hobart, Australia. In addition to supporting our underway pCO_2 measurements, they are also collecting samples for carbon isotope measurements (Quay) and DIC and nutrients (Tilbrook). For this reason, we have combined resources to place ship riders on each of the cruises. They maintain the underway systems and collect the discrete samples. The cruise data can be obtained from our website located at**:** http://www.pmel.noaa.gov/co2/uwpco2.

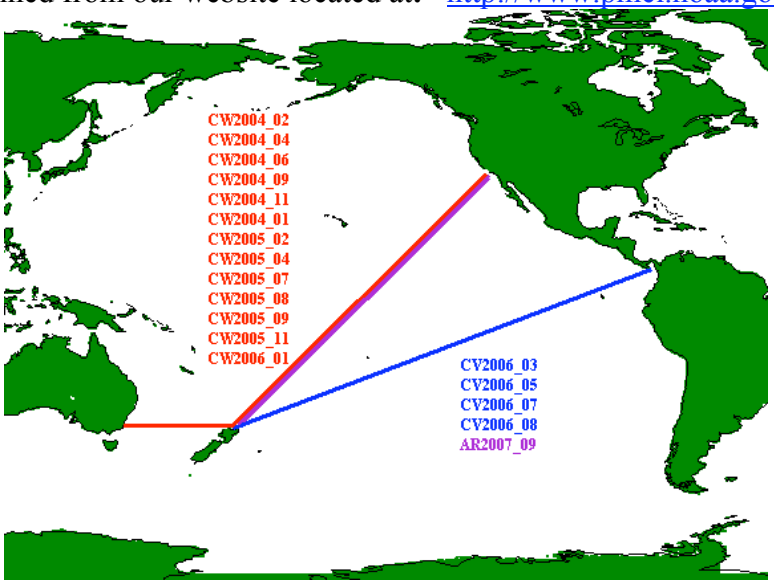

Figure 8:Cruise Tracks of the Columbus Waikato (red), Cap Victor (blue) and Albert Rickmers (purple) occupied during FY2004-2007.

A summary of the cruise results from Fall 2005 thru September 2007 is shown in *Figure 9* **Error! Reference source not found.**and *Figure 11***Error! Reference source not found.**. The results show strong seasonal variability of CO_2 fluxes in the southern and northern subtropic, but out of phase by 6 months. The most recent data shows high seawater pCO_2 values due to La Niña conditions in the equatorial Pacific. These results are described in the AGU/ASLO abstract by Cosca et al., (2008). The data will undergo further contextual checks by LDEO scientists before it is submitted to CDIAC for archiving.

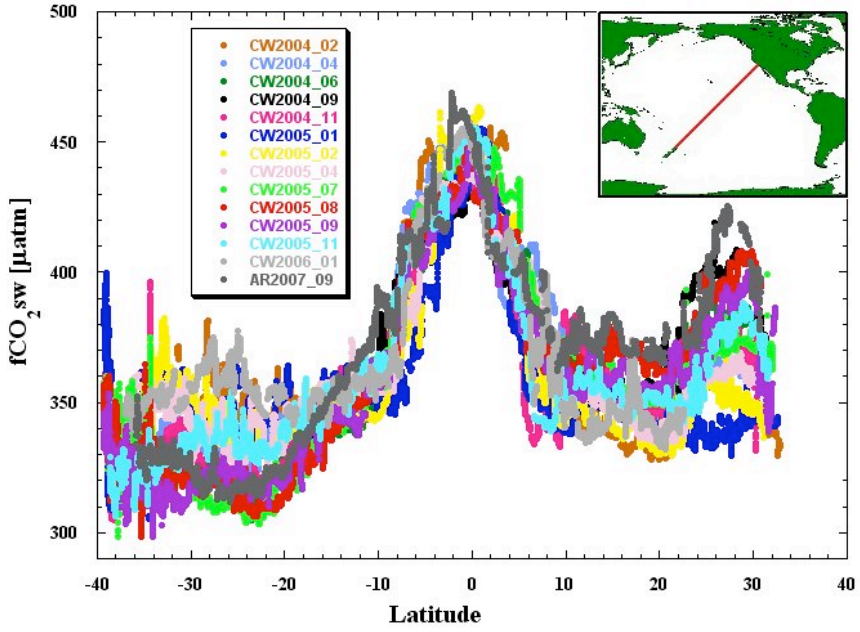

Figure 9:Time-Series of surface water pCO2 levels in the tropical and subtropical Pacific Resulting from Columbus Waikato and Albert Rickmers repeat observations from 2004 to 2007.

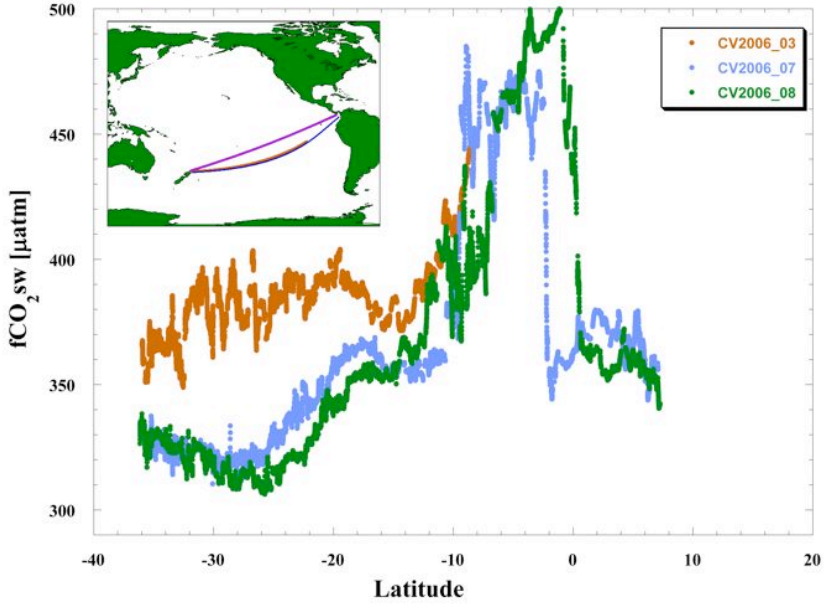

Figure 11:. Time-Series of surface water pCO2 levels in the tropical and subtropical Pacific Resulting from Cap Victor repeat observations in 2006.

RVIB *Palmer*- LDEO lead

Description:

We have operated successfully a semi-automated surface water pCO_2 system aboard the RVIB *Nathaniel Palmer* with vital operational assistance from the Raytheon Polar Support group. Since RVIB Palmer, an ice-breaking research vessel is one of the few research ships which are operated in high latitude areas of the Southern Ocean even during winter months, our CO_2 program aboard this vessel allows us to make observations in hostile environments of the high latitude oceans, where deep and intermediate water masses are formed in winter. Our pCO_2 system has been upgraded completely two years ago with the support from NOAA, and some new modifications are being added in order to make the system more stable and reliable. As the data are obtained, they are processed and added to our global database.

The locations of our data obtained since the beginning of this project in 2001 are shown in ***Figure 13***. The total number of surface water pCO_2 data obtained since January 2001 is 592,425. Approximately 48,524 measurements were added to the database during the calendar year 2007

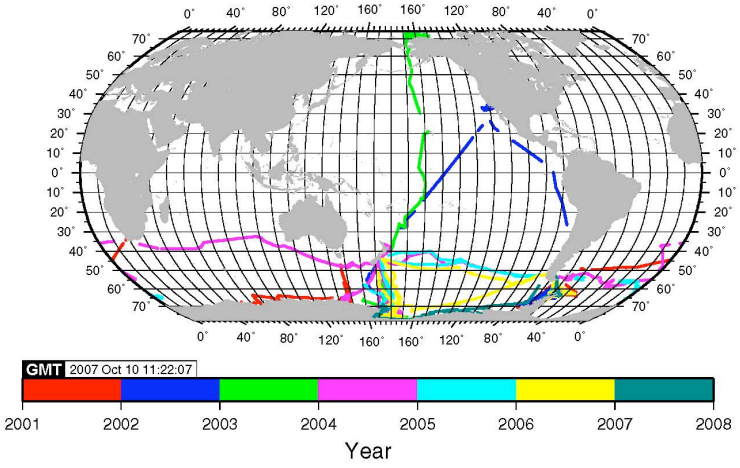

Figure 13: The locations of surface water pCO2 measurements made aboard the RVIB Palmer since 2001. The dark green lines indicate the observations made during the calendar year 2007, during which about 48,524 pCO2 measurements were obtained.

Cruise ship *Explorer of the Seas*-AOML lead

Causes for non-return: Some loss of data occurred because of a buildup of salt in the return line from the dry box to the equilibrator and water trapped in the tubing between the headspace pump and the dry box blocking the sample gas flow. Slow flushing of lines means that we omit data from the first 10-minutes after the standard run.
Description: Last year, after four years of sailing in the Caribbean the ship changed its route to sail to Bermuda during the summer time with alternating cruises from New York to Bermuda and the Eastern Caribbean. New York is now the permanent port for the ship and sails not only to Bermuda and the Caribbean but also to Canada and New England during the summer. This yields excellent temporal and spatial coverage. The area has been used as a test bed to create flux maps utilizing remote sensing (see research highlights). During the performance period a near-real time data display was instituted where daily pictorial updates of concentrations along the cruise track in color-code like in *Figure 15* below and a display of temperatures and concentrations are provided on the website: http://www.aoml.noaa.gov/ocd/gcc/explorer_realtime.php for system checks and quality control. During the performance period all weekly data was combined into yearly data files for the particular routes (East, West, and North). The yearly data and metadata in IOCCP recommended format from 2003-2006 has been submitted to CDIAC.

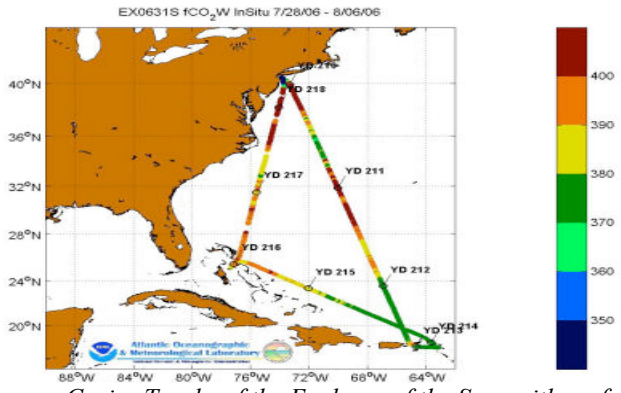

Figure 15: One of the Summer Cruise Tracks of the Explorer of the Seas with surface water pCO2 levels for late summer 2006.

Container Ship *Skogafoss*- AOML & RSMAS lead

Causes for non-return: This system has run unattended or with untrained observers except for 3 cruises when AOML were onboard. Data gaps have occurred for a variety of reasons, including failure by ship's personnel to open the seawater valves and malfunctioning gas flow sensors. On the last cruise, the CO_2 analyzer water channel drifted out of calibration, causing negative water concentrations to be registered. Although the effect on the CO_2 concentration is small, the data had to be flagged for caution.

Description: The *Skogafoss* sails between Iceland and Boston.and covers a critical high latitude region that has been shown to be a large CO_2 sink. Large seasonal variations are observed as shown in *Figure* ***16***. During the early spring, pCO_2 values well above atmospheric levels are measured over most of the ocean transect due to entrainment of deep water to the surface. In late spring, values decrease significantly as a result of high biological productivity during this time. The *Skogafoss* did its last transit in May of 2007 and is expected to be replaced by a permanent ship later this year. The system will be re-installed as soon as it happens so that we can continue the measurements on the same line.

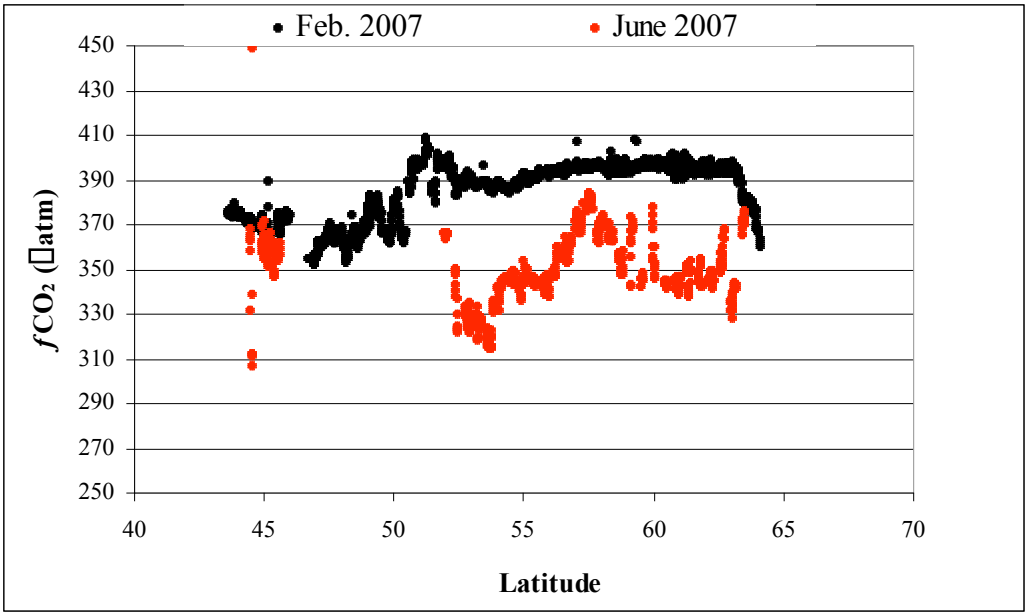

Figure 16: pCO_2 levels along the transect of the Skogafoss in February 2007 and June 2007

Container Ship *Oleander*- BIOS lead

Description: The MV *Oleander* crosses weekly between New Jersey and Hamilton, Bermuda. Given the ~100 crossings a year, this gives excellent temporal and spatial coverage of the North Atlantic subtropical gyre, Gulf Stream, middle Atlantic Bight and coastal zone. The MV *Oleander* transits the region of Subtropical Mode Water (STMW) formation during the winter southeast of the Gulf Stream, and the highly productive coastal zone of the Eastern Seaboard.

Data Return:

The pCO_2 system was installed on the MV *Oleander* in February 2006. Over the year, the total data collected was ~108,000, with a ~68% data recovery. The remaining 32% had some caveats associated with flow rates through the Licor. The MV *Oleander* system uses a LiCOR 7000 NDIR detector, and there are a few minor unresolved issues of comparability to systems with a LiCOR 6262 NDIR detector. Maintenance of the pCO_2 system has become relatively routine with weekly visits to the ship during the ship's turnaround in Hamilton, Bermuda. Our group has developed a good rapport with the ship officers, engineers and crew, and their good will has contributed greatly to the success of the system installation on the ship.

The seawater and atmospheric pCO_2 data from 2006 and 2007 (up to May) have been submitted to LDEO. We are in the process of preparing the metadata information and data QC/QA for submission of data to CDIAC in yearly reports (i.e., 2006, 2007). The seawater and atmospheric pCO_2 data will also be served at the following site (http://www.bios.edu/Labs/co2lab/vos.html).

Causes for non-return:

On the MV *Oleander*, the primary causes for non-return have been associated with ship-related issues (seawater pump system turned off; delays getting on to the ship); failure of the waste reservoir and delays related to component replacement. Over the last year there have been occasions when the seawater system were not turned on during the weekly turnaround of the ship. There have also been several occasions when our group has not been

able to access the ship in port due to offload/onload pressures when the ship is undertaking very quick turnarounds due to weather delays. On a couple of occasions, the pump that drains seawater from the waste reservoir has failed and we have had delays in replacing the pump. The equilibrator is located in the Engine Room near the seawater system and TSG. It is located ~5' below the water line, requiring the equilibrator waste seawater to free drain into a waste reservoir, which in turn is drained by a pump back into the seawater line downstream of the tap off to the pCO_2 system. In 2007, the pump has failed twice with shutdown of the system after overflow into the ship's bilges. Recently, we have added a second, stronger pump to ensure that the waste water is pumped overboard. The primary filter on the seawater intake line has also needed to be cleaned each week; otherwise rust and debris from the *Oleander*'s internal plumbing clogs the line and slows the flow rate into the equilibrator. We have also had problems with the Superlogic Module boards; these modules have had to be replaced. The condenser tubes have clogged with salt crystals causing a shutdown of the system. The condenser tubes have been replaced

The average temperature of the engine room has been ~47°C with the CPU failing in 2006 due to temperatures over 60°C. We have modified the dry box, adding new fans, and replaced the CPU with one that has a higher temperature threshold (80*C) with no problems since. The replacement of the CPU caused a problem with the GPS comport that is currently being addressed. The engine room air is quite dirty requiring cleaning of all filters each week..

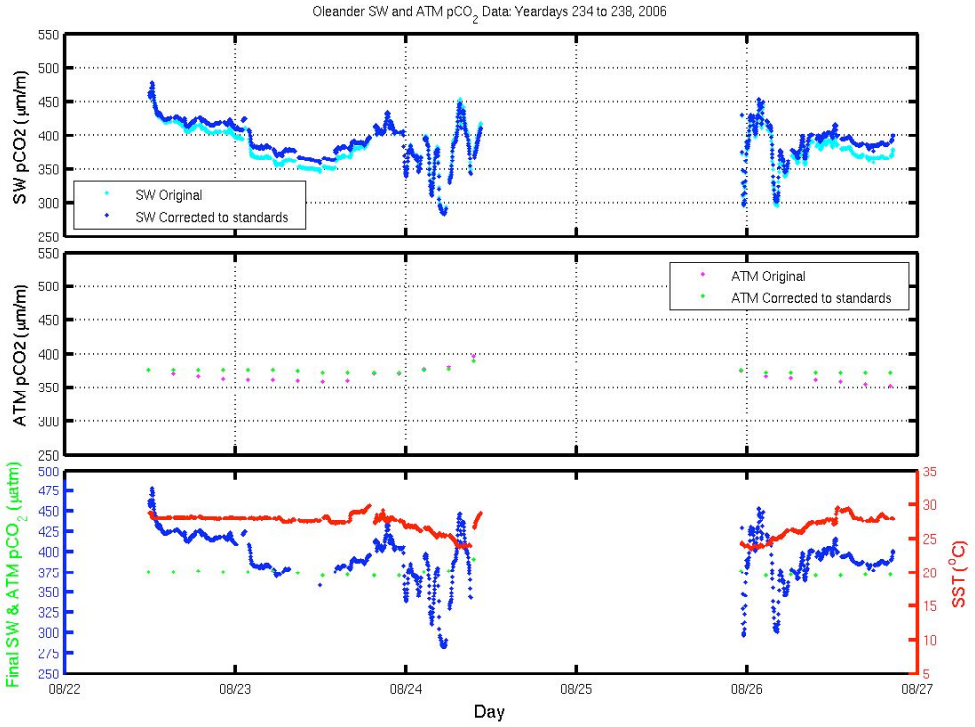

Figure 17: Example of Oleander data during a crossing from New Jersey to Bermuda, and back again in August 2006. The data gap is when the ship on 8/25 was in port

R/V *Atlantic Explorer* - BIOS lead

Description: The R/V *Atlantic Explorer* operates in the North Atlantic Ocean (zone NA6), servicing four oceanographic time-series (e.g., Bermuda Atlantic Time-series Study, Hydrostation S, Bermuda Testbed Mooring, Ocean Flux Program) and other research projects. This data stream provides groundtruthing pCO_2 datasets for the subtropical gyre of the North Atlantic Ocean. In 2007, the *Atlantic Explorer*has been scheduled for 173 days.

Data Return:

The pCO_2 system was installed on the RV *Atlantic Explorer* in April 2006. Over the last 16 months, the total data collected was ~92,000, with a ~83% data recovery. The

remaining 17%% were flagged due to problems associated with the Valco multi-position valve and distribution of standards through the system, and delays in replacing the standards.Maintenance of the pCO_2 system has become relatively routine during the ship's turnaround at the BIOS dock. The seawater and atmospheric pCO_2 data from 2006 and 2007 (up to May) have been submitted to LDEO. We are in the process of preparing the metadata information and data QC/QA for submission of data to CDIAC in yearly reports (i.e., 2006, 2007). The seawater and atmospheric pCO_2 data will also be served at the following site (http://www.bios.edu/Labs/co2lab/vos.html).

Causes for non-return:

In 2007, the major problem with the *Atlantic Explorer* system has been intermittent problems with the Valco multiposition valve. The valve has been replaced. We have had problems with the Ivisco valve that controls the flushing of the lines with freshwater. This valve has failed twice due to salt crystal buildup. We have also had problems with clogging of the flow meter impeller. We have also had problems with the Superlogic Module boards due to faulty power feed; these modules have had to be replaced. The acrodisk have also been clogged and in need of regular cleaning. We have also had a few problems with the GPS system, with a faulty 232 to 485 converter, and faulty comport.

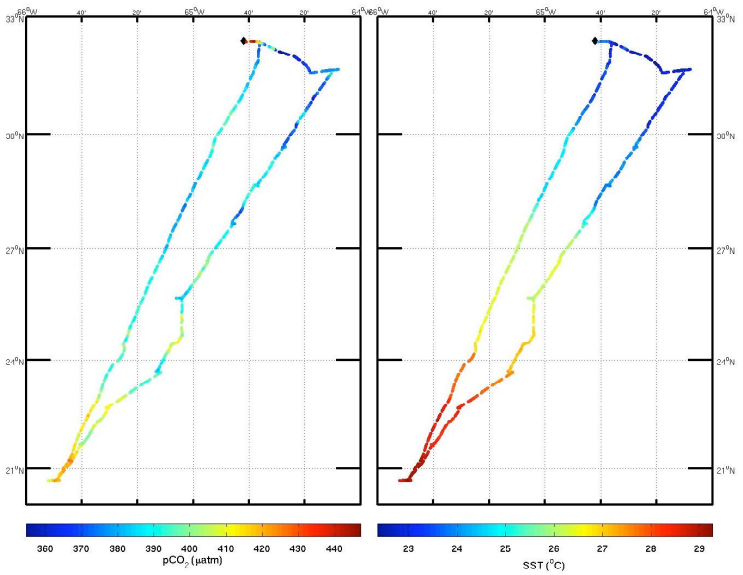

Figure 18:Example of Atlantic Explorer data during a transect across the North Atlantic subtropical gyre in May 2006.

Adherence to monitoring principles

The efforts of the NOAA VOS pCO_2 group have met the important monitoring principle of uniform instrumentation with a quantifiable accuracy. All systems are calibrated with

standards that are traceable to the WMO scale. The first units were delivered in the summer of 2003, within a year of receipt of program funding. We are actively involved in assuring uniform instrumentation, through close interactions including organizing training session for customers with the manufacturer General Oceanics who is building instruments to our specifications, uniform operating protocol, and uniform data reduction procedures.

Data management and dissemination:

An important part of the VOS effort is to disseminate quality controlled data to the community at large in an expedient fashion.

For the thermosalinograph data the AOML/GOOS group developed a data quality control computer code using OpenSource, FreeSoftware and multiplatform solutions, which allow great freedom for the future of the project. It injects the data into a PostgreSQL database where it is then subjected to different quality control procedures. Probably the major advantage to have the dataset in a relational database, such as PostgreSQL, is the use of indexes for fast sub samples by any criteria, for example QC flags, range limits, time windows or grouped values by sensors or area or ships. This way, virtually infinite metadata sets could be created from the same real dataset but with the same storage demand and a small development effort. We are planning to install a DAP server, which will allow the direct access to the database from traditional scientific tools, such as MatLab, Python, Grads, Ferret, and others. The core of the system management is done in Python, which has modules for the direct database access, scientific procedures and easily deal with dates. One of the many advantages is that it allows for a robust and fast development. The reduced data is then submitted to a full automatic quality check, were the initial check is redone on the reduced data. Additionally, it allows comparisons with other measurements, such as from profiling floats, XBTs, and climatology. Every 6 hours the GTS is updated with the new reduced approved data. The capability to transmit data to the Coriolis center and NODC are under development. Details on each of the quality control steps can be found in : *www.aoml.noaa.gov/phod/tsg/data/qc_sheet.pdf.*

The PMEL group wrote new software to quickly process data files that are transmitted daily via iridium satellite from the Ka'imimoana and Albert Rickmers. This software processes the daily data and creates diagnostic plots of pCO_2, temperature, salinity, barometric pressure, water flow and gas flow. The plots are posted on a newly created internal website and are used as a diagnostic tool for data processing and quality control of the underway pCO_2 data. All current and previous VOS data files are quality controlled using the data submission protocol for ships under the NOAA Office of Climate Observations (OCO) workplan "pCO_2 measurements from ships".
The LDEO group, in close interaction with the data acquisition groups, oversees shipboard quality control so that the quality of data and consistency is monitored for the whole group. The participants of the VOS program are able to access the data which are listed in a uniform format. For this purpose, the LDEO group established an open web site at the following URL: http://www.ldeo.columbia.edu/CO2. The site provides not only the

numerical data, but also maps showing the ship's tracks for each data file. The new data will be accessible only to the VOS participants for a period of three years, and will be sent to the Carbon Dioxide Information and Analysis Center (CDIAC), Oak Ridge, TN, for the permanent archiving and distribution to the public after this period. This close coupling of the data acquisition with data processing/evaluation and interpretation will guarantee high quality field observation data.

As a part of the VOS program, the LDEO group processed and added to its database the measurements from the 2 other field operations; 1) the R/V Laurence M. Gould, which is supported by NSF as a part of the Long-Term Research in Environmental Biology (LTRE) program in the Drake Passage area, Southern Ocean; 2) Yacht Turmoil in coastal waters. The sampling locations during the R/V L. M. Gould program are shown in ***Figure 19***. A total of approximately 35,718 pCO_2 measurements that were made aboard the R/V Gould during the calendar year 2007 have been added to the database. This makes a total of 337,097 pCO_2 measurements for the Gould program from March, 2002 through September, 2007.

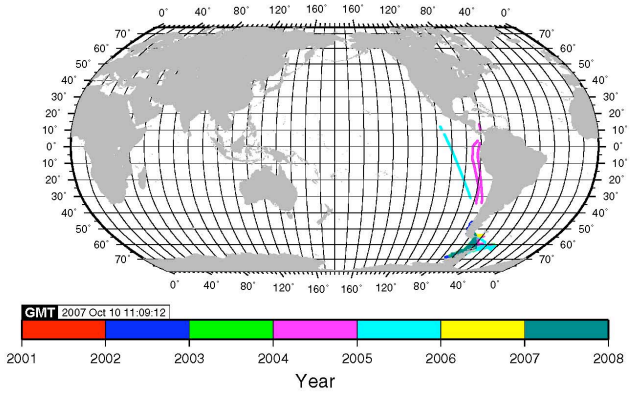

Figure 19: The locations of the surface water pCO2 measurements obtained aboard the R/V Gould during this project, March, 2002 through August, 2007. The years of the measurements are color coded.

During the performance period two important data products were submitted to CDIAC. A compilation of coastal data from this group and other investigators was provided that is the cornerstone for the chapter 17 of the SOCCR report (*Chavez and Takahashi, 2006*). All the data that are used for the global pCO_2 climatology comprised of 3.3 million data points was sent to CDIAC as well.

CDIAC has just implemented a Live Access Server (LAS) for the data with funding from a companion effort. The LAS at http://cdiac3.ornl.gov/underway/servlets/dataset is being populated. Investigators, and the oceanographic community use the data extensively. This data is also used for national and international assessments such as the IPCC.

<u>Research highlights;</u>

1. It is widely recognized that robust methods to interpolate CO_2 measurements in time and space are needed to produce CO_2 flux maps from measurements along a line. Publications by *Lueger et al.* (2006) for the North Atlantic and *Wanninkhof et al.* (2007) for the Caribbean Seas show how temperature can be utilized to produce regional flux maps. The algorithms are area specific but show a robust predictive capacity and provide a way to utilize remote sensing to produce flux maps with high spatial and temporal resolution. The data used to create the algorithms were obtained on the ships funded under this effort.

2. Data obtained as part of the CO_2 on ships effort has been extensively used in the recently submitted paper by Takahashi et al. (2007) "Climatological Mean and Decadal Change in Surface Ocean pCO_2, and Net Sea-air CO_2 Flux over the Global Oceans". Takahashi and colleagues were the first to produce a monthly air-sea CO_2 flux climatology based on surface water CO_2 data. An updated climatological mean distribution for the surface water pCO_2 over the global oceans in non-El Niño conditions has been constructed with spatial resolution of 4° (latitude) x 5° (longitude) for a reference year 2000 based upon about 3 million measurements of surface water pCO_2 obtained from 1970 to 2006. The database used for this study is about 3 times larger than the 0.94 million used for our earlier paper (Takahashi et al., 2002). A global ocean database for a single reference year 2000 is assembled using this mean rate for correcting observations made in different years to the reference year. The annual mean for the contemporary net CO_2 uptake flux over the global oceans is estimated to be -1.4 ± 0.7 Pg-C yr^{-1}. Taking the pre-industrial steady state ocean source of 0.4 ± 0.2 Pg-C yr^{-1} into account, the total ocean uptake flux including the anthropogenic CO_2 is estimated to be -1.8 ± 0.7 Pg-C yr^{-1} in 2000.

3. As part of our continuing effort to understand decadal changes in the carbon fluxes of the equatorial Pacific, we developed seasonal and interannual pCO2-SST relationships from shipboard data that were applied to high-resolution temperature fields deduced from satellite data to obtain high-resolution large-scale estimates of the regional fluxes. The data were gathered onboard research ships from November 1981 through September 2007. The data were collected during repeat transects of the equatorial Pacific between 95°W and 165°E, and included five El Niño periods (1982–1983, 1986–1987, 1991–1994 and 1997–1998 and 2002–2003) and four La Niña periods (1988–1989, 1995–1996, 1998–2000 and 2007). Data were collected during the warm boreal winter-spring season (January through June) and during the cooler boreal summer-fall season (July through December) of each year making it possible to examine the interannual and seasonal variability of the fCO2-SST relationships. A linear fit through the data sets yields an inverse correlation between SST and fCO2, with both interannual and seasonal differences in slope. In particular, the results indicate a strong interannual El Niño – Southern Oscillation (ENSO), Pacific Decadal Oscillation (PDO) and weaker seasonal variability. There is also a slight increase (~27%) in the out-gassing flux of CO2 after the 1997–1998 PDO mode shift. Most of this increase is due to increase in wind speeds after the spring of 1998. These increases are consistent with the recent rebound of the shallow water meridional overturning circulation in the tropical and subtropical Pacific after the PDO shift. In the summer of 2007, equatorial pCO2 values were extremely high, likely resulting from the development of La Niña conditions in the late summer of 2007.

4. Using the observations made since the 1970's we have investigated increases in pCO_2 in surface water in the North Pacific Ocean. In 19 areas that are located in the open North Pacific, the surface water pCO_2 values have been increasing at a rate similar to the mean atmospheric CO_2 increase of about 1.5 ppm/yr. Although surface waters are out of equilibrium with atmospheric CO_2 because of the seasonal swing of SST, biological production and deep-water upwelling, the ocean surface waters appear to take up CO_2 from the air keeping up with the atmospheric CO_2 increase. In contrast, in four areas located near and within the Bering and Okhotsk Seas, the surface water pCO_2 have been decreasing with time, in spite of the fact that surface water temperatures have been increasing. This may be attributed to an increase in photosynthesis in the high latitude North Pacific, that has been reported by Gregg et al. (2003) on the basis of remote-sensed ocean colors. (Reference: Takahashi et al., 2006)

5. The VOS CO_2 data is providing valuable information on CO_2 variability in surface seawater over a wide range of time- and spatial scales that have not been fully examined. In 2006, both BIOS' ships collected high frequency data in the region of the subtropical gyre of the North Atlantic Ocean, Gulf Stream, Middle Atlantic Bight and coastal ocean of the eastern seaboard.

   Comparisons of underway seawater pCO_2 data collected from BIOS's ship, R/V Atlantic Explorer with the BTM pCO_2 sensor have been initiated (*Figure **20***). Over 15,000 seawater pCO_2 datapoints were collected from the Atlantic Explorer within 80 km of the BTM in 2006. Seawater pCO_2 data collected from the R/V Atlantic Explorer underway system within 10 km of the BTM (also within 3 minutes of each BTM datapoint) had an average difference of less than 0.5 µatm.

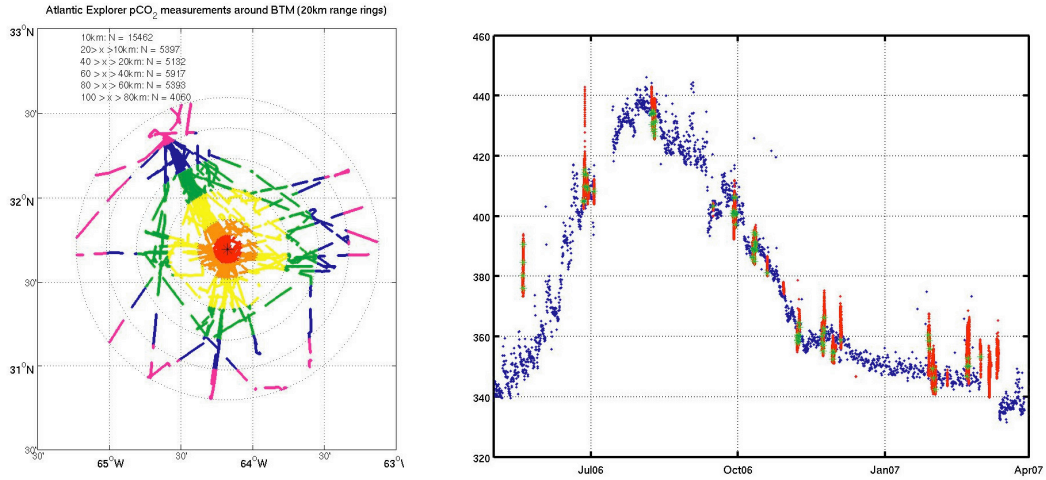

Figure 20. Left Panel. Seawater pCO2 data collected from the RV Atlantic Explorer within 80 km of the BTM site (64.2°W, 31.7°N). Red zone indicates data collected within 10 km of the BTM. Right Panel. Comparison of R/V Atlantic Explorer seawater pCO2 data (red data) with BTM pCO2 sensor data (blue data). The AE data was collected within 10 km of the BTM. The green datapoints indicate AE data collected within 3 minutes of each BTM datapoint.

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